



United States Patent Application for

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**ELECTROCHEMICAL DEPOSITION OF CARBON NANOPARTICLES FROM ORGANIC SOLUTION**

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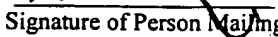
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ELECTROCHEMICAL DEPOSITION OF CARBON  
NANOPARTICLES FROM ORGANIC SOLUTIONS

This invention relates to nanoparticles including both nanotubes and nanofilaments  
5 and more particularly relates to carbon nanoparticles deposited by the electrochemical  
deposition from organic solutions and claims the benefit of priority to United States  
Provisional Application Serial No. 60/284,360 filed on April 17, 2001.

BACKGROUND AND PRIOR ART

10 Currently, carbon nanoparticles including both nanotubes and nanofilaments are  
found in extended commercial applications in modern technologies, for example, for the  
manufacture of composite materials, nanoscale machines, flat-panel displays, and computer  
memory devices. The wide application of carbon nanotubes is based on their unique physical  
and mechanical properties, which show the high electrical and thermal conductivity, and high  
15 strength values along the nanotubes' axis. In the direction perpendicular to the fiber axis,  
these values are very low.

Carbon nanotubes are oftentimes produced by vapor phase deposition on particles of  
transition metals such as Fe, Ni, and Co in chemical vapor deposition (CVD) reactor(see  
United States Patent 6,146,227 by Mancevski wherein the metal catalysts decompose the  
20 hydrocarbides and aid in the deposition of the ordered carbon), by electrochemical deposition  
of the catalyst followed by CVD at high temperatures (see United States Patent 6,129,901 by  
Moskovits et al), by catalytic plasma enhanced CVD, or by a carbon arc-discharge process.

In recent years, more and more attention is being paid to the electrochemical  
deposition technique for the manufacture of electronic devices because the electrochemical  
25 deposition method is simple, low in capital equipment cost, and can be easily scaled to large  
scale production.

It would be very important to develop a low temperature, simple process capable of  
substantial production of nanotubes.

### SUMMARY OF THE INVENTION

The first objective of the present invention is to provide carbon nanotubes from a liquid phase.

5 The second objective of the present invention is to provide carbon nanotubes at a reduced cost.

Another objective of the present invention is to provide carbon nanotubes on an enlarged scale of production.

A preferred embodiment of the invention is the preparation of carbon nanotubes comprising the steps of: providing an electrochemical bath of an organic solution of  
10 methanol and benzyl alcohol disposed between and in contact with silicon wafers coated with iron and nickel particles as electrodes; imposing a direct current potential of approximately 1000 volts between said electrodes; and providing a current density of approximately 12 milliamps per square centimeter between said electrodes for a time sufficient that carbon nanotubes of up to approximately 50  $\mu\text{m}$  are developed.

15 Further objects and advantages of this invention will be apparent from the following detailed description of a presently preferred embodiment which is illustrated schematically in the accompanying drawings.

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### BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 shows a schematic of the electrochemical deposition apparatus for carrying out the process of the invention.

Fig. 2 shows 4 stages in the growth of the nanofilaments.

25 Fig. 3 shows carbonaceous deposits including nanofilaments from the process of the invention.

Fig. 4 shows TEM images of the nanoparticles filaments including hollow structures.

Fig. 5 graphs the EDS spectrum of the carbon nanofilaments.

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### DESCRIPTION OF THE PREFERRED EMBODIMENT

Before explaining the disclosed embodiment of the present invention in detail it is to be understood that the invention is not limited in its application to the details of the particular arrangement shown since the invention is capable of other embodiments. Also, the terminology used herein is for the purpose of description and not of limitation.

It would be useful to discuss the meanings of some words used herein and their applications before discussing the novel process of the invention for producing carbon nanotubes including:

SEM- scanning electron microscope

TEM – transmitting electro microscope

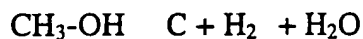
Nanotubes – a particle having a hollow body and lengths of from approximately 2 to approximately 10 nano meters

Nanofilaments – a solid particle having lengths of from approximately 2 to approximately 10 nano meters

The method of the invention is based on the discovery that it is possible to create nanoparticles including nanofilaments and nanotubes at ambient temperatures by electrochemical decomposition of an organic system in the presence of catalysts such as iron and nickel.

Refer now to Figure 1 which presents a schematic representation of the preferred embodiment of the electrochemical deposition apparatus for producing the carbon nanotubes. Electrochemical decomposition of the liquid hydrocarbon 14 takes place in a preferably cylindrical (or any other shape) reaction vessel 16 made of glass or ceramic. The power supply 18 with an ammeter 20 and voltmeter 22 is connected between the anode 24 and cathode 26. Agitation of the liquid is provided with a magnetic stirrer 28 separated from the liquid by a spacer 30. A reference electrode 32 is provided to monitor the electrochemical activity.

The preparation of the carbon nanoparticles which include both nanofilaments and nanotubes is by a catalytic facilitated electrochemical decomposition of an organic solution at ambient temperatures. The decomposition is according to the 2 simultaneous reactions which follow:



$\text{C}_6\text{H}_5\text{CH}_2\text{-OH} \quad 7\text{C} + 3\text{H}_2 + \text{H}_2\text{O}$ . which results in the growth and deposition of nanoparticles on the catalytic coated substrates serving as electrodes for the electrochemical reaction.

5           The nano catalyst particles preferred for use in this invention are produced by evaporating a mixture of nickel and iron in argon onto the silicon substrate at a pressure of a few torrs (approximately 0.01 atmospheres) to produce particulates of from approximately 2 to approximately 10 nano meters deposited onto the substrate.

10           Reference should now be made to Fig. 2, which shows the four stages in the growth of the nanofilaments on the catalytic coated cathodes during the electrochemical deposition process. The decomposition of the two liquids provides carbon as seen from the two simultaneous chemical reactions which carbon 1(a) deposits on the catalytic particles; 2(b) diffuses into the catalysts; 3(c) grows into a carbide deposit; and 4(d) develops into nanoparticles which are both filaments and tubes.

15           The process according to this invention utilizes a reaction carried out in a glass container holding a solution of approximately 7 to approximately 40 %, preferably approximately 30 %, of methanol in benzene alcohol at ambient temperature and a current density of approximately 12 mA/cm<sup>2</sup> between silicon wafers as the electrodes coated with nanoparticles of equal amounts of iron and nickel ranging from approximately 2 to  
20 approximately 10 nano meters and separated by approximately 5 mm with a voltage potential imposed between them of approximately 1000 volts direct current.

The useful parameters of the inventive process follows:

- 25 (a) the process temperature, although broadly defined as ambient, ranges from approximately 10 to approximately 80, preferably approximately 15 to approximately 60, optimally approximately 20 to approximately 30, degrees C.
- (b) the current density ranges from a broad range of approximately 5 (10<sup>4</sup>) to 5 approximately (10<sup>5</sup>), preferably 2 approximately (10<sup>5</sup>), dc volts / meter.
- (c) the suitable ambient pressure for electrochemical decomposition of the carbon containing solution according to the invention is about 1 atmosphere.

(d) useful substrates as anodes and cathodes include electrically conductive metals of which silicon and stainless steel are exemplary with silicon being the preferred metal which is highly useful in the process of this invention.

5 (e) the preparation of useful catalysts and particle size ranges is best understood from the article by F. Halperin entitled "Quantum size effects in metal particles" which appeared in the Review of Modern Physics, Vol. 58, No. 3 pp. 533-608 (in particular see page 589) and include the metals iron, cobalt and nickel. The preferred catalysts for this invention are nano particulates of iron and nickel disposed on a silicon electrode having nano diameter sizes ranging from approximately 2 to approximately 10 nano meters.

10 The carbon nanofilaments and nanotubes prepared by the inventive process can be seen by reference first to: Fig. 3 which shows carbonaceous deposits including nanofilaments from the process of the invention: then on to Fig. 4 which shows TEM images of the nanofilaments including hollow structures; and, finally to Fig. 5 which graphs the EDS spectrum of the carbon nanofilaments.

15 The deposition of carbon nanoparticles by the inventive electrochemical ambient process has occurred both as bundled and web-like nanofilaments with: the bundle diameters ranging from approximately 50 to approximately 100 nm and lengths of up to approximately 10nm; and, the web-like diameters ranging from approximately 50 to approximately 200 nm and lengths of approximately 30 to approximately 50nm.

20 The disclosed invention makes it possible to produce nanoparticles in a low temperature process. The resulting advantages are many-fold. Firstly, this approach allows the process to be simplified, low cost and readily scaled up at reduced cost. Secondly, many different substrates can be used as the electrode onto which the nanoparticle catalysts are deposited.

25 While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here  
30 appended.